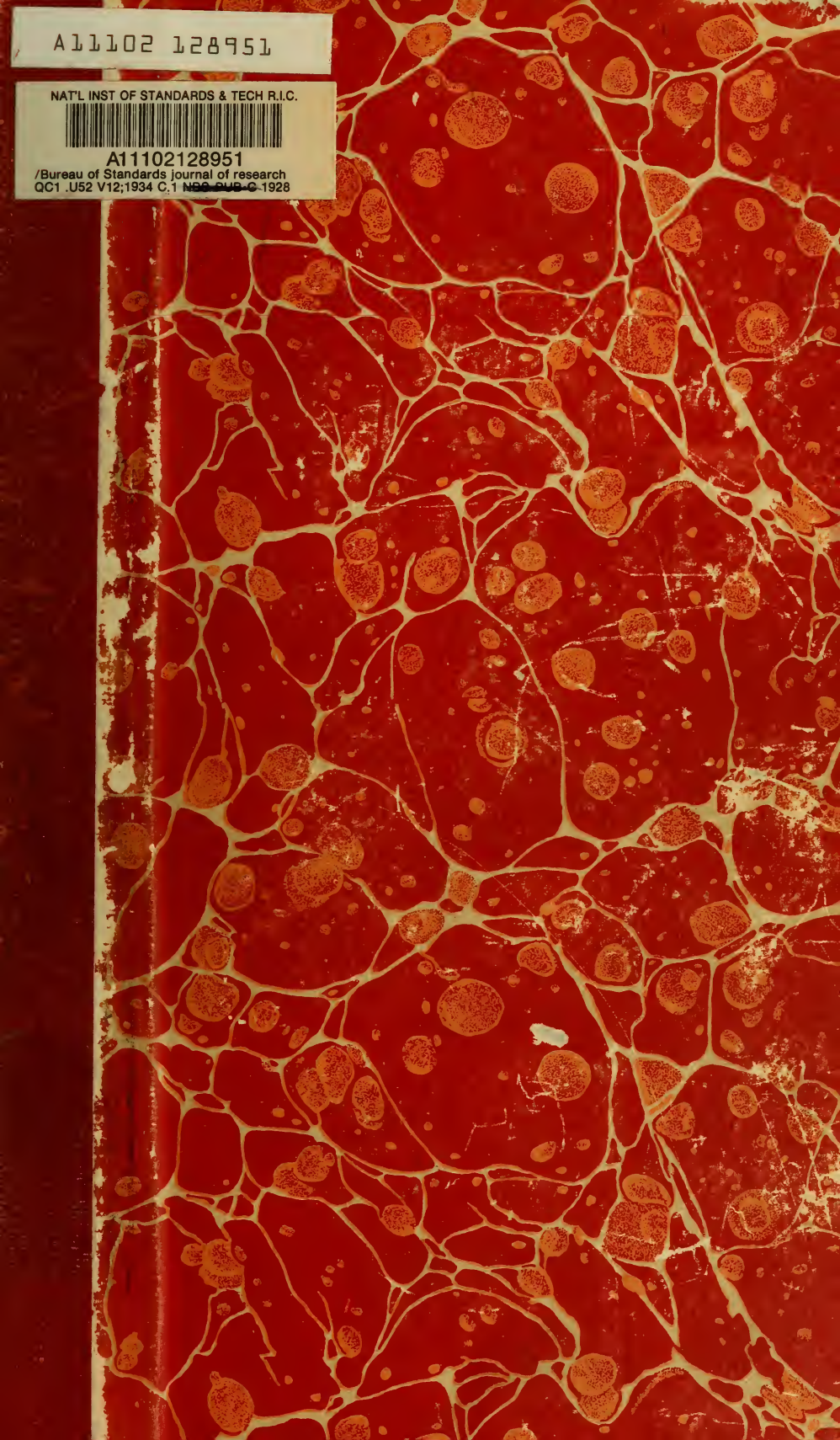
A11102 128951

NAT'L INST OF STANDARDS & TECH R.I.C.

A11102128951

/Bureau of Standards journal of research
QC1 .U52 V12;1934 C.1 NBS PUB C 1928



U.S. Department of Commerce, Bureau of Standards

RESEARCH PAPER RP655

Part of Bureau of Standards Journal of Research, vol. 12, March 1934

METHODS FOR THE SEPARATION OF PLATINUM, PALLADIUM, RHODIUM, AND IRIDIUM FROM ONE ANOTHER AND FOR THEIR GRAVIMETRIC DETERMINATION

By Raleigh Gilchrist

ABSTRACT

A method is described for the analytical separation of platinum from each or all of the three metals, palladium, rhodium, and iridium. It is based upon the complete precipitation of the hydrated dioxides of palladium, rhodium, and iridium in a boiling solution containing sodium bromate and having an acidity of pH 6. Two precipitations of the hydrated dioxides were found to be sufficient to effect the quantitative isolation of platinum.

The separation of palladium from rhodium and iridium, by means of dimethylglyoxime, and its subsequent determination are also described. The procedure for the separation of rhodium from iridium by titanous chloride and for the determination of these two metals, given in detail in a previous publication from this laboratory, is discussed only briefly in this paper.

CONTENTS

		Page
I.	Introduction	291
II.	Materials used in the experiments	293
III.	Separation of platinum from palladium, rhodium, and iridium	293
	1. Method recommended for the separation of platinum from palladium, rhodium, and iridium, either collectively or singly	294
	(*a*) Preparation of the solution	294
	(*b*) Hydrolytic precipitation of palladium, rhodium, and iridium	294
IV.	Discussion of the hydrolytic procedure	295
V.	Determination of platinum	296
VI.	Determination of palladium	298
VII.	Determination of rhodium and of iridium	299
VIII.	Experimental results on the separation of platinum from palladium, rhodium, and iridium	300
IX.	Separation of palladium from rhodium and iridium	302
X.	Separation of rhodium from iridium	303

I. INTRODUCTION

In a systematic scheme for the analysis of the platinum group, it is the usual procedure to remove osmium and ruthenium first as volatile tetroxides and then to effect the separation of the four remaining

platinum metals from one another. It has been the practically universal custom to effect these latter separations by means of potassium chloride or ammonium chloride. These reagents produce relatively insoluble compounds of the type K_2PtCl_6, $(NH_4)_2IrCl_6$, etc., with the quadrivalent platinum metal chlorides and soluble compounds with the ter- and bi-valent chlorides. In spite of the general use of potassium chloride or of ammonium chloride to effect the separation of iridium from rhodium, or of platinum from rhodium, or of platinum from iridium, these reagents can hardly be expected to produce clean-cut separations. Experience in this laboratory with the purification of the platinum metals has shown that rhodium contaminates iridium, when the latter is precipitated as ammonium chloroiridate, and that it can be completely eliminated only with great difficulty, if at all, by repeated precipitation of the iridium. Rhodium likewise contaminates platinum, when the latter is precipitated as ammonium chloroplatinate. Since the potassium and the ammonium salts of the quadrivalent platinum metal chlorides are slightly soluble, a small amount of iridium or of platinum must remain in solution, thereby contaminating the very metal from which complete separation is sought. This situation, unfortunately, is often disregarded. Even though the separations are followed by treatment of the metal residues with acids or with molten potassium bisulphate, again a sharp separation cannot be expected. In using such methods of separation, it often becomes necessary to combine the determinations of a number of separate fractions in evaluating the determination of a particular constituent.

The importance of hydrolytic reactions in analytical separations appears to have been given but little attention by chemists in the past. The reason for this may possibly be a lack of means for carefully controlling the pH of the solutions. It is evident that hydroxides of the platinum metals were known, but their significance in analysis does not seem to have been realized. The precipitation of hydrated tervalent rhodium oxide by alkalies and by alkali carbonates, for instance, was well known, but no use was made of the reaction in the analytical separation of rhodium. In the purification of platinum, Doebereiner [1] did propose a method by which the impurities were collectively precipitated by hydrolysis, using milk of lime. Claus,[2] however, pointed out that the elimination of impurities by this method was never complete. About 20 years ago, Mylius and Mazzucchelli [3] proposed a similar collective precipitation of impurities for use in the approximate analysis of platinum, except that an oxidizing reagent, sodium hypobromite, was added to a neutral or slightly alkaline solution to produce hydrated oxides of higher valence. Precipitation by hydrolysis was later studied by Wichers [4] in the development of an analytical method for the separation of rhodium from platinum and in the refining of platinum.[5] In the analytical separation, a definite alkalinity was established by the addition of an excess of freshly prepared barium carbonate. In the refining operation, precipitation was made in a solution slightly alkaline with sodium bicarbonate to which sodium bromate was added. These researches of Wichers

[1] Franz Doebereiner, Ann., vol. 14, pp. 17, 251, 1835.
[2] C. Claus, Bull. acad. sci., St. Petersburg, vol. 3, p. 38, 1845.
[3] F. Mylius and A. Mazzucchelli, Z. anorg. Chem., vol. 89, p. 1, 1914.
[4] E. Wichers, Jour. Am. Chem. Soc., vol. 46, p. 1818, 1924.
[5] E. Wichers, R. Gilchrist, and W. H. Swanger, Trans. Am. Inst. Mining Met. Eng., vol. 76, p. 602, 1928.

clearly demonstrated the value of hydrolytic reactions in the chemistry of the platinum metals.

The use of hydrolytic precipitation was further extended by Gilchrist in studies on the analytical separation and determination of ruthenium,[6 7] osmium,[8] and iridium.[9] In these studies, it was found that ruthenium is completely precipitated from a boiling solution having an acidity of pH 6;[10] that osmium is quantitatively precipitated between pH 1.5 and 6; and that iridium is entirely precipitated between pH 4 and 6.

Quite recently, Moser and Hackhofer[11] have reported on the separation of iridium from platinum, and Moser and Graber[12] on the separation of rhodium from platinum, by a hydrolytic procedure in which the alkalinity is fixed by the reaction between bromate and bromide ions. This reaction, however, appears to come to equilibrium so slowly that prolonged boiling and digestion is required to complete the precipitation.

The purpose of this paper is to present the results of the application of hydrolytic precipitation to the separation of rhodium from platinum, of iridium from platinum, of palladium from platinum, and of the collective separation of rhodium, iridium, and palladium from platinum. In addition, the paper contains the results of experiments on the determination of palladium, as well as its separation from rhodium and iridium, by means of dimethylglyoxime.

II. MATERIALS USED IN THE EXPERIMENTS

The platinum metals which were used throughout the investigation were purified by methods previously described[13] and were found to be free from impurities by spectrochemical analysis. In order to avoid errors incident to volumetric measurements, weighed portions of the ammonium salts of the chloro-acids of rhodium and of iridium were used. The compounds were carefully mixed by grinding in an agate mortar and their metallic contents determined by direct ignition of portions of the salts in hydrogen, whenever a series of samples was weighed. The metallic contents were never calculated from the theoretical compositions of the salts. With platinum and palladium, weighed portions of the pure metals in the form of foil were taken.

III. SEPARATION OF PLATINUM FROM PALLADIUM, RHODIUM, AND IRIDIUM

The simplest and most direct way to separate platinum from palladium, rhodium, and iridium is to precipitate collectively by hydrolysis the hydrated oxides of palladium, rhodium, and iridium. The method recommended for this separation is given below and is equally suitable for the separation of platinum from each of the other three metals when present singly with platinum.

[6] Gilchrist, B.S. Jour. Research, vol. 3, p. 993, 1929.
[7] Gilchrist, B.S. Jour. Research, vol. 12, p. 283, 1934.
[8] Gilchrist, B.S. Jour. Research, vol. 6, p. 421, 1931.
[9] Gilchrist, B.S. Jour. Research, vol. 9, p. 547, 1932.
[10] It is to be noted that the values of pH mentioned in this paper were determined by means of indicator solutions and were not corrected to correspond to readings of the hydrogen electrode.
[11] L. Moser and H. Hackhofer, Monatsh., vol. 59, p. 44, 1932.
[12] L. Moser and H. Graber, Monatsh., vol. 59, p. 61, 1932.
[13] See footnote 5, p. 292.

1. METHOD RECOMMENDED FOR THE SEPARATION OF PLATINUM FROM PALLADIUM, RHODIUM, AND IRIDIUM, EITHER COLLECTIVELY OR SINGLY

(a) PREPARATION OF THE SOLUTION

Evaporate the solution, containing platinum, palladium, rhodium, and iridium, to a moist residue on the steam bath in a 600-ml beaker. Add 5 ml of hydrochloric acid [14] and again evaporate, repeating this operation until nitroso-compounds are decomposed. Add 2 g of sodium chloride and 5 ml of hydrochloric acid and evaporate this time to dryness. Add 2 ml of hydrochloric acid and dilute the solution to 300 ml with water.

(b) HYDROLYTIC PRECIPITATION OF PALLADIUM, RHODIUM, AND IRIDIUM

Heat the resulting solution to boiling and add to it 20 ml of a filtered 10 percent solution of sodium bromate. Carefully add a filtered 10 percent solution of sodium bicarbonate until the dark green solution shows evidence of the formation of a permanent precipitate. Test the acidity of the solution by allowing a drop of brom cresol purple indicator solution (0.04 percent) to run down the stirring rod into the drop which clings to it as it is lifted from the hot solution. Sufficient bicarbonate has been added when the color of the indicator changes from yellow to blue. At this stage, add 10 ml more of the bromate reagent and boil the solution gently for 5 minutes. Test the acidity of the solution again and adjust it to that specified above, if necessary. The tendency is for the pH of the solution to shift to the acid side of the indicator as hydrolysis of the platinum metal compounds progresses. Again add 10 ml of the bromate solution and boil gently for 15 minutes. During this treatment, the acidity of the hot solution should stay constant.

As a precautionary measure, it is well to test the acidity again at the end of the second boiling period. On removing the beaker from the source of heat, the precipitate which has been formed will settle quickly, leaving a yellow mother liquor containing the platinum. Filter [15] the solution. Pour the supernatant liquid through first, then transfer the precipitate. Rinse the beaker, without attempting to remove material which clings to the walls, and wash the precipitate with a hot 1 percent solution of sodium chloride. It is important that the acidity of the wash solution be tested before it is used because hydrated palladium dioxide is attacked somewhat by hot slightly acid solutions. A solution of sodium chloride whose acidity does not exceed that at which brom cresol purple indicator contained in it changes color can be safely used. If the precipitate is caught on filter paper, return the filter to the beaker and dissolve the hydrated dioxides in

[14] Throughout this paper, whenever acids are mentioned, hydrochloric acid will mean the concentrated acid of specific gravity 1.18; nitric acid, the concentrated acid of specific gravity 1.42; and sulphuric acid, the concentrated acid of specific gravity 1.84. Diluted acids will be designated as follows: For example, diluted hydrochloric acid (1+99) will mean one volume of the concentrated acid of specific gravity 1.18 diluted with 99 volumes of water.

[15] The solution may be filtered through paper. It is highly desirable, however, to avoid paper if the palladium, rhodium, or iridium is to be reprecipitated. Iridium dioxide, which dissolves much less readily than either palladium or rhodium dioxide, tends to stain the paper pulp and cannot always be removed by washing. The material of which the paper is composed undoubtedly reacts with acids to some extent and, as a consequence, small quantities of organic compounds of the platinum metals appear to be formed which are not easily hydrolyzed. The difficulties encountered with filter paper are avoided by using a porcelain filtering crucible, having glazed walls and a porous base. Such crucibles are made by the State Porcelain Works, Berlin, Germany. The ones used in this work were 45 mm in height, 40 mm in diameter at the top and had a capacity of 30 ml. While no information could be obtained regarding their degree of porosity, they bore the mark "A1" and were very satisfactory. No trace of the precipitates was ever detected to have escaped these filters. No doubt, glass crucibles of suitable porosity could also be used.

diluted hydrochloric acid (1 + 1). If the filtering crucible is used, place it with the stirring rod in the beaker used for the precipitation. It may be necessary to remove a small amount of the precipitate which has crept over the lip of the beaker. This may be done with a very small piece of filter paper and added to the beaker. Replace the watch glass and add from 10 to 20 ml of hydrochloric acid, pouring a portion of it into the crucible and the remainder into the beaker. Place the covered beaker on the steam bath. The rhodium and palladium compounds will dissolve quickly. The iridium compound will dissolve more slowly and may even require a drop of nitric acid to be added to the solution. Carefully lift the crucible with the stirring rod, wash it with water and place in in a 250-ml beaker. The porous bottom will be stained somewhat. Add about 5 ml of hydrochloric acid, again pouring a portion of the acid into the crucible. Cover the beaker with a watch glass and set it on the steam bath. This treatment will usually leach out the small quantity of metal chloride present in the porous bottom. This operation should be repeated once more with fresh acid, however, to insure complete removal of metal chloride.

Combine the leachings with the main portion of the solution, add 2 g of sodium chloride, and evaporate to dryness on the steam bath. Add 2 ml of hydrochloric acid, dilute the solution to 300 ml with water, and repeat the precipitation of the hydrated dioxides as directed above. Two such precipitations have been found sufficient to separate platinum from rhodium, palladium, and iridium.[16]

IV. DISCUSSION OF THE HYDROLYTIC PROCEDURE

The normal valence of rhodium in chloride solution is three; that of iridium, three or four; that of palladium, two; and that of platinum, owing to the conditions necessary to dissolve it, four.

When a solution of tervalent rhodium as halide or sulphate is neutralized, the rhodium precipitates as a yellow hydrated tervalent oxide. This compound does not settle well and has a tendency to become colloidal when washed. For these reasons, the quantitative handling of it is somewhat difficult. If, on the other hand, the rhodium is oxidized to the quadrivalent state, it can be precipitated as an olive-green hydrated dioxide which does settle rapidly and which displays no tendency to become colloidal. It was found that complete precipitation of the olive-green compound occurred at pH 6 in a boiling solution.

The precipitate of hydrated tervalent iridium oxide is somewhat flocculent and gelatinous, whereas the deep green hydrated dioxide is more granular and settles quickly from solution. It was found that the dioxide is completely precipitated from a boiling solution over a range of acidity, pH 4 to 6.

[16] In the experiments reported in section VIII of this paper, the ratio of platinum to rhodium was approximately 5 to 1, that of platinum to palladium 2.5 to 1, and that of platinum to iridium 1 to 1. The quantity of platinum present was usually about 250 milligrams. In the Pt–Rh separation, no platinum was found in the rhodium solutions after the second hydrolytic precipitation, and in only one of the five experiments was any rhodium detected in the platinum fractions. The quantity detected in this instance was less than 0.1 mg. In the Pt–Pd separation, no palladium was detected in the recovered platinum nor was any platinum found in the filtrates from the precipitation of the palladium with dimethylglyoxime. In the Pt–Ir separation, only one of the three platinum fractions appeared to contain any iridium. The amount of iridium, however, was much less than 0.1 mg. For certain work in which a high degree of accuracy in the platinum determination is not essential, a single hydrolytic precipitation may be sufficient. It must be borne in mind, however, that a small amount of platinum will contaminate the hydrolytic precipitate. When careful work is being done, it may be necessary to make a third hydrolytic precipitation, but only in unusual cases.

Hydrated palladium dioxide, obtained in the presence of bromate, is brown in color, is completely precipitated at pH 6, and likewise settles well from solution.

Owing to the possible interference of nitroso compounds, it is recommended that the solution first be evaporated several times with hydrochloric acid. On a number of occasions when solutions containing rhodium had not been so treated, a small amount of rhodium failed to precipitate on hydrolysis. When the solutions were evaporated with hydrochloric acid, complete precipitation was always obtained. Unless the solution contains a sufficient amount of sodium chloride, it should not be evaporated to dryness. A solution containing only rhodium chloride, for instance, when evaporated to dryness on the steam bath, forms brown scales which do not redissolve readily in water. If sodium chloride is present, a double salt is formed which is easily soluble.

In the precipitation of rhodium and of palladium, sodium bromate is added to the slightly acidified solution. This is done to prevent the precipitation of tervalent rhodium and bivalent palladium oxides when the bicarbonate is added. Some of the bromate is decomposed by the acid solution so that it is advisable to add this reagent at intervals. A hot solution of tervalent iridium can be neutralized to pH 6 without the formation of a precipitate. In the recovery of iridium from a pure solution, it is often convenient to neutralize to pH 6 before adding the bromate. As the bicarbonate solution is added to the acidified bromate solution, an olive-green precipitate appears with rhodium, a dark green one with iridium, and a brown one with palladium. These precipitates immediately redissolve, particularly those of rhodium and palladium, but, as the acidity is reduced, permanent precipitates form. The appearance of a coagulated precipitate is a convenient indication that the acidity of the solution is approaching the desired value, namely, pH 6. Owing to the deep color of the solution, the endpoint cannot be determined in the usual manner. A convenient method, however, consists in testing a drop of the hot solution, clinging to the stirring rod, with a drop of brom cresol purple indicator solution. The actual acidity of the solution will be slightly greater than that indicated by the drop. Experiments have repeatedly shown, however, that precipitation is quantitative at the acidity determined in this manner.

It sometimes happens that the salt used in preparing the wash solution contains a small amount of acid. Hydrated iridium dioxide can be safely washed with solutions as acid as pH 4. Hydrated rhodium dioxide, and more particularly the palladium compound, are attacked by slightly acid solutions and should be washed only with solutions which are practically neutral. It is well, therefore, to test the acidity of the wash solution before using it. A solution more acid than that which causes a change in color of brom cresol purple indicator contained in it should not be used.

V. DETERMINATION OF PLATINUM

The following procedure is recommended for the recovery and determination of platinum, after its separation from palladium, rhodium, and iridium.

Add 20 ml of hydrochloric acid to each of the cooled filtrates from the hydrolytic precipitation. Warm the solutions carefully until

they become quiescent. Combine the partially concentrated filtrates and then evaporate to dryness. To make certain that all of the bromate is decomposed, add 5 ml of hydrochloric acid and again evaporate. Dissolve the residue in 100 ml of water and filter the resulting solution. Wash the filter with diluted hydrochloric acid (1 + 99). Add 20 ml of hydrochloric acid and dilute the solution to 400 ml.

Precipitate the platinum as sulphide from a gently boiling solution by passing a rapid stream of hydrogen sulphide through it. Allow the solution to cool somewhat with the hydrogen sulphide still passing through it.

Filter the solution and wash the sulphide precipitate with diluted hydrochloric acid (1 + 99). Ignite the dried filter and precipitate in a porcelain crucible. Leach the metal residue with diluted hydrochloric acid, transfer it to a filter, and wash it thoroughly with hot water. Ignite the filter and metal again strongly in the air. It is usually customary to weigh the metal so obtained. A slight error will result, however, because sulphur cannot be entirely eliminated by ignition either in air or in hydrogen. The amount of sulphur retained by 0.25–g portions of platinum is usually less than 1 milligram.

In work of the highest accuracy, dissolve the metallic platinum obtained by ignition of the sulphide in aqua regia. Decompose nitroso compounds by adding hydrochloric acid and evaporating to a moist residue. Filter the solution into a clean, unetched beaker. Wash the filter with diluted hydrochloric acid (1 + 99). Dilute the solution to 100 ml, heat it to boiling, and add to it a solution containing 3 g of sodium acetate and 1 ml of formic acid for each 0.25 g of platinum present. Boil the resulting solution gently until the precipitated metallic platinum is well coagulated and the supernatant liquid is colorless. Filter the solution and wash the metallic deposit with a hot 1 percent solution of ammonium chloride. Place the filter and the spongy metal in a porcelain crucible and ignite them strongly in the air. Leach and wash the ignited metal as previously directed. This precaution is taken to remove traces of soluble salts. Finally ignite the platinum again in air. It will now be free from sulphur. Weigh as metallic platinum.

In the determination of the platinum metals, by ignition of sulphide precipitates, a significant error may be caused by the retention of sulphur. It is well known that when palladium sulphide is ignited elimination of sulphur is very difficult to attain. In fact, if the sulphide is ignited rapidly enough, it will often fuse into a silvery globule. While the retention of sulphur by platinum is not nearly so marked as it is by palladium, a small but significant amount does remain when the sulphide is ignited in air. In 17 experiments, the weights of platinum recovered by ignition of the sulphide in air exceeded those taken by amounts which ranged from 0.0 to 1.1 mg and averaged 0.5 mg. In 14 of the 17 experiments, the platinum residues were recovered after separation from palladium, rhodium, and iridium. In the other three, pure platinum was dissolved in aqua regia and simply precipitated by hydrogen sulphide. These three residues were alternately ignited in air and in hydrogen. The excesses in weight dropped from 1.1 mg, 0.5 mg, and 0.7 mg to 0.6 mg, 0.2 mg, and 0.4 mg, respectively, by this treatment. These 3 residues and 4 others were then dissolved in aqua regia and the resulting solutions evaporated several times with hydrochloric acid. The solutions were filtered and to each of them

was added 5 drops of a filtered 10 percent solution of barium chloride. A precipitate of barium sulphate was obtained in each solution. No precipitate of barium sulphate was observed in blank solutions which contained the same quantities of nitric and hydrochloric acids.

Wichers,[17] a few years ago, found errors of the same magnitude, when similar quantities of platinum sulphide were ignited in air. When he charred and ignited the filters and precipitates extremely slowly, however, no significant errors were observed and the platinum residues were found to contain only a few hundredths of a milligram of sulphur. When he recovered the platinum with formic acid, the results were consistent with those reported in this paper. Wichers also extended his observations to the ignition of rhodium sulphide. He found no significant amount of sulphur in the resulting residues nor did he find that the manner of ignition, whether rapid or slow, affected the weight of the recovered metal. These conclusions were later confirmed by the writer.

VI. DETERMINATION OF PALLADIUM

Since the introduction of dimethylglyoxime as a precipitant for palladium by Wunder and Thüringer,[18] thisorganic compound has practically, if not entirely, displaced reagents formerly used, such as mercuric cyanide and potassium iodide. Wunder and Thüringer, according to their original articles, ignited the compound of palladium with dimethylglyoxime to metal for purposes of weighing. Soon, however, it became customary to weigh the dried compound as is done in the case of nickel.

The preparation of palladium in the metallic form suitable for weighing has always been attended by the difficulty which arises from the pronounced property of palladium to absorb hydrogen. When palladium is determined as metal, Swanger [19] recommended the decomposition of the dried glyoxime precipitate in a Rose crucible under hydrogen, followed by an ignition in air and another in hydrogen. In order to eliminate the absorbed hydrogen, he heated the crucible again in air for a moment, and finally reduced the slightly oxidized metal with formic acid on the hot plate. The treatment with formic acid often has to be repeated several times in order to produce a sponge which does not have a slight purplish color.

According to Wöhler,[20] palladium dioxide, PdO_2, cannot exist above 200 C, but decomposes into the monoxide, PdO, and oxygen. The monoxide, in turn, has a dissociation pressure of 760 mm at 877 C. Experiments showed that metallic palladium, silvery grey in color, can be obtained by simply igniting in carbon dioxide for 2 minutes the palladium which has been reduced in hydrogen. It was also found that the same result was obtained by igniting oxidized palladium in carbon dioxide. It was further found that simple strong ignition of oxidized palladium in the air formed the metal, which, however, took on a purplish color as it cooled to room temperature. The quantity of oxide thus formed was found to amount to only 0.1 mg with portions of palladium weighing 100 mg.

[17] Unpublished work by Edward Wichers.
[18] M. Wunder and V. Thüringer, Z. anal. Chem., vol. 52, pp. 101, 660, 740, 1913.
[19] W. H. Swanger, Analysis of Dental Gold Alloys, B.S. Scientific Papers No. 532, Aug. 11, 1926.
[20] L. Wöhler, Z. Elektrochem., vol. 11, p. 836, 1905.

Three experiments were made in which the glyoxime precipitate was caught on filter paper, washed with diluted hydrochloric acid (1 + 99), and finally with hot water. The filter containing the precipitate was wrapped in a second filter and charred carefully in the air. The residue was then ignited strongly in the air and the resulting oxidized palladium reduced in hydrogen. Finally, the metal was heated in carbon dioxide for 2 minutes and allowed to cool in an atmosphere of this gas. The quantities of palladium taken, in the form of foil, were 0.0994 g, 0.0992 g, and 0.1009 g. The metal residues weighed 0.0995 g, 0.0993 g, and 0.1010, respectively, no correction being made for the filter paper ash.

Experiments were also made in which the glyoxime compound itself was weighed. One of the precipitates was caught on an asbestos pad in a Gooch crucible and the other two in porcelain filtering crucibles. The precipitates were washed thoroughly with hot water and dried for 1 hour at 110 C. The quantities of palladium taken, in the form of foil, were 0.1061 g, 0.0954 g, and 0.0973 g. The glyoxime precipitates weighed 0.3348 g, 0.3014 g, and 0.3072 g. Using the theoretical factor for the percentage of palladium in the compound, namely, 0.3167, the calculated quantities of palladium recovered were 0.1060 g, 0.0954 g, and 0.0973 g, respectively.

In the preceding experiments, the palladium was precipitated from solutions of its chloride in diluted hydrochloric acid. Each solution had a volume of 350 ml and contained 10 ml of hydrochloric acid. No palladium was detected in the filtrates nor in the wash waters. In another experiment, the glyoxime precipitate was washed with 200 ml of hot water in order to determine whether it was appreciably soluble. No palladium was detected in the evaporated washings.

Other experiments showed that palladium was quantitatively precipitated by dimethylglyoxime not only from solutions of its chloride in diluted hydrochloric acid but also from solutions of its sulphate in diluted sulphuric acid. When the yellow precipitate was decomposed by nitric acid or by aqua regia, as is often done when palladium is to be reprecipitated, it was found that the metal was not always completely recovered. A small but significant amount of it remained in solution, which could be precipitated only after the filtrate had been heated until vapors of sulphuric acid were evolved.

VII. DETERMINATION OF RHODIUM AND OF IRIDIUM

Rhodium may be conveniently determined by igniting the hydrated dioxide to an anhydrous oxide in air and reducing the latter compound to metal in hydrogen. In order to prevent deflagration, the filter and precipitate are impregnated with ammonium chloride and carefully charred before they are strongly ignited in the air.

Rhodium may also be conveniently determined by igniting the sulphide to an anhydrous oxide and reducing the resulting oxide to metal in hydrogen. This method is recommended for the recovery and determination of rhodium after its separation from iridium by titanous chloride.[21] Rhodium is quantitatively precipitated by hydrogen sulphide from a gently boiling solution of its chloride in diluted hydrochloric acid, but it is only partially precipitated from a

[21] See footnote 9, p. 293.

solution of its sulphate in diluted sulphuric acid. A solution of the rhodium can be prepared, however, by adding diluted hydrochloric acid (1+2), equal to three times the volume of the concentrated sulphuric-acid solution, and boiling it. The yellow color of the sulphate solution then changes to rose-red, no doubt indicating a conversion of the sulphate to the chloride. No difficulty attends the precipitation of rhodium from the solution so treated.

Iridium is best determined by igniting its hydrated dioxide to an anhydrous oxide and then reducing the oxide in hydrogen. The same precaution must be used to prevent deflagration as was described for rhodium. Unfortunately, the precipitation of iridium from acid solutions by hydrogen sulphide is often incomplete and as yet the conditions suitable for quantitative precipitation have not been established.

VIII. EXPERIMENTAL RESULTS ON THE SEPARATION OF PLATINUM FROM PALLADIUM, RHODIUM, AND IRIDIUM

The method which is outlined in section III was used to effect the separation of platinum from palladium; the separation of platinum from rhodium; the separation of platinum from iridium; and the separation of platinum from these three metals when present together.

Owing to the difficulty encountered in the direct precipitation of the platinum from the hydrolytic filtrates by formic acid, the platinum was first precipitated by hydrogen sulphide. The ignited sulphide was redissolved and the platinum then precipitated by formic acid in a solution buffered with sodium acetate, as described in section V.

1. SEPARATION OF PLATINUM FROM PALLADIUM

The results of the determination of platinum and of palladium, starting with solutions containing both metals, are given in table 1. The hydrated dioxide of palladium from the second hydrolytic precipitation was redissolved in hydrochloric acid. The glyoxime precipitate was ignited in air, then in hydrogen, and finally in carbon dioxide. The palladium was determined as metal. No palladium was detected with dimethylglyoxime in the dissolved platinum residues nor was any platinum found, by means of ammonium chloride, in the filtrates from the precipitation of the palladium with dimethylglyoxime.

TABLE 1.—*Results of the analysis of solutions containing platinum and palladium*

Analysis no.	Platinum taken	Platinum recovered	Error	Palladium taken	Palladium recovered	Error
	g	*g*	*g*	*g*	*g*	*g*
25-701	0.2848	0.2849	+0.0001	0.1044	0.1043	−0.0001
26-702	.2793	.2794	+.0001	.1243	.1243	.0000

If palladium alone is to be separated from platinum, a single hydrolytic precipitation, followed by a single precipitation with dimethylglyoxime, is undoubtedly sufficient to effect complete

separation. Complete separation of the two metals can also be accomplished, no doubt, by a double precipitation with dimethylglyoxime alone, provided that certain precautions are observed. Wunder and Thüringer,[22] operating in a hot solution, encountered difficulty in separating palladium from platinum with dimethylglyoxime, but Davis [23] later showed that if palladium is precipitated in a cold solution two precipitations as the glyoxime compound remove the platinum. Swanger [24] subsequently followed the procedure of Davis with excellent results. It should be borne in mind, however, that, if the palladium is reprecipitated from a solution of the first precipitate in nitric acid or in aqua regia, a small amount of palladium may remain in solution.

2. SEPARATION OF PLATINUM FROM RHODIUM

The results of the determination of platinum and of rhodium, starting with solutions containing both metals, are given in table 2. The rhodium was recovered by precipitation with hydrogen sulphide and determined as metal.

TABLE 2.—*Results of the analysis of solutions containing platinum and rhodium*

Analysis no.	Platinum taken	Platinum recovered	Error	$(NH_4)_3RhCl_6$ taken	Rhodium present [1]	Rhodium recovered	Error
	g	*g*	*g*	*g*	*g*	*g*	*g*
9-646	0.2450	[2] 0.2454	+0.0004	0.1537	0.0469	0.0468	−0.0001
10-647	.2350	[2].2350	.0000	.1682	.0513	.0512	−.0001
18-652	.2469	.2469	.0000	.0953	.0291	.0291	.0000
19-653	.2479	.2479	.0000	.0800	.0244	.0243	−.0001
20-654	.2617	.2618	+.0001	.0968	.0295	.0296	+.0001

[1] Calculated on the basis of an experimentally determined rhodium content of 30.50 percent.
[2] Pt determined by ignition of sulphide.

NOTE.—In analyses nos. 9-646 and 10-647, filter paper was used to catch the hydrated dioxide. In the other 3 experiments, the porcelain filtering crucible was used. In none of the 5 rhodium solutions, previous to the recovery of rhodium, was any platinum detected. The test for platinum was made as follows: The second hydrolytic precipitate of rhodium dioxide was dissolved in hydrochloric acid and the resulting solution evaporated to a moist residue on the steam bath. 5 ml of hydrochloric acid was added and the solution diluted somewhat and filtered. The filter was washed with diluted hydrochloric acid (1+99). The rhodium solution was then evaporated to a small volume and to it was added 10 drops of a saturated solution of ammonium chloride and 2 or 3 drops of nitric acid. The solution was next carefully evaporated to dryness on the steam bath. The dry salt mixture was dissolved in the smallest quantity of water possible and allowed to stand for one half hour. In the solutions tested, no precipitate of ammonium chloroplatinate appeared, whereas, in solutions of known platinum content 0.1 mg of platinum was readily detected and a precipitate was formed with 0.05 mg of platinum. A very faint trace of rhodium was detected in the final platinum residue of analysis no. 10-647. No rhodium was detected in the other 4 platinum residues. The test for rhodium was made as follows: The platinum residues were dissolved in aqua regia, the solutions were evaporated to a sirup with hydrochloric acid, and the bulk of the platinum was precipitated with ammonium chloride. The mother liquors and the wash waters containing ammonium chloride were evaporated to dryness. An extremely small amount of rhodium, if present, produces under these conditions a greenish discoloration of the small amount of ammonium chloroplatinate which has been carried along with the wash waters.

In determining rhodium, when it alone has been separated from platinum, it may be more convenient to catch the precipitate from the second hydrolysis on filter paper. The hydrated dioxide of rhodium can be ignited to metal in the same manner as iridium dioxide. If palladium or iridium is present with the rhodium, it is recommended that the rhodium be recovered, after its separation from these metals, by precipitation with hydrogen sulphide.

[22] See footnote 18, p. 298.
[23] C. W. Davis, Separation of Palladium from Platinum by Means of Dimethylglyoxime, Bur. Mines Reports of Investigations, serial no. 2351, May 1922.
[24] See footnote 19, p. 298.

3. SEPARATION OF PLATINUM FROM IRIDIUM

The results of the determination of platinum and of iridium, starting with solutions containing both metals, are given in table 3. The iridium was recovered by hydrolytic precipitation and determined as metal.

TABLE 3.—*Results of the analysis of solutions containing platinum and iridium*

Analysis no.	Platinum taken	Platinum recovered	Error	$(NH_4)_2IrCl_6$ taken	Iridium present [1]	Iridium recovered	Error
	g	*g*	*g*	*g*	*g*	*g*	*g*
21-611	0.2359	0.2358	−0.0001	0.4500	0.1944	0.1945	+0.0001
22-612	.2692	.2694	+.0002	.4721	.2039	.2040	+.0001
23-613	.2501	.2501	.0000	.5684	.2455	.2456	+.0001

[1] Calculated on the basis of an experimentally determined iridium content of 43.20 percent.

NOTE.—The filtrates from the precipitation of platinum by hydrogen sulphide and by formic acid were heated until vapors of sulphuric acid were evolved and tested for iridium by adding nitric acid. In this test, with quantities of iridium less than 0.1 mg, the color developed is green, with larger amounts it is blue. Owing to the incomplete precipitation of iridium by hydrogen sulphide and by formic acid, iridium, if present with the platinum, will appear in the filtrates from these precipitations, at least partially. The filtrates from analysis no. 21-611 showed the presence of a quantity of iridium much less than 0.1 mg. No iridium was detected in the filtrates from the other 2 experiments.

4. SEPARATION OF PLATINUM FROM THE THREE METALS, PALLADIUM, RHODIUM, AND IRIDIUM

Critical experiments were made in which palladium, rhodium, and iridium were simultaneously precipitated as hydrated dioxides in the presence of platinum. The resulting platinum filtrates were carefully examined for palladium, rhodium, and iridium and the absence of these metals was established. The third hydrolytic filtrate gave no evidence of the presence of platinum, when treated with ammonium chloride.

That no platinum contaminated the second hydrolytic precipitate of the mixed dioxides of rhodium and iridium was shown by the following experiment: From a solution containing 0.2642 g of platinum, 0.1385 g of iridium, and 0.0465 g of rhodium, 0.0464 g of rhodium was recovered after its separation from iridium by treatment with titanous chloride, as described in a previous publication.[25] The ash of the paper used to filter the solution of rhodium sulphate, produced by dissolving the metallic rhodium from the second precipitation with titanous chloride, was found to contain no platinum. If platinum had contaminated the hydrolytic precipitate, it would have appeared, at least in part, at this point in the analysis.

IX. SEPARATION OF PALLADIUM FROM RHODIUM AND IRIDIUM

In one of their papers Wunder and Thüringer [26] reported on the separation of palladium from rhodium and from iridium, by means of dimethylglyoxime.

Preliminary experiments in this laboratory showed that palladium, when precipitated by dimethylglyoxime from a solution of the mixed precipitate of hydrated dioxides in diluted hydrochloric acid, was not contaminated by either rhodium or iridium. Apparently, a single precipitation of the glyoxime compound sufficed to effect a clean

[25] See footnote 9, p. 293.
[26] M. Wunder and V. Thüringer, Z. anal. Chem., vol. 52, p. 660, 1913.

separation. To confirm this observation, two solutions were prepared containing in the one, 0.2300 g of iridium, 0.0177 g of rhodium and 0.0342 g of palladium, and in the other, 0.2154 g of iridium, 0.0112 g of rhodium and 0.0333 g of palladium.

The palladium precipitates were caught on filter paper, washed with diluted hydrochloric acid (1 + 99), and finally with hot water. The filters and precipitates were placed in 500-ml erlenmeyer flasks and decomposed by treatment with 5 ml of sulphuric acid to which portions of nitric acid were added. After destruction of organic matter, the solutions were heated until heavy vapors of sulphuric acid were evolved. The solutions were then diluted somewhat and filtered. The filters were washed with diluted hydrochloric acid (1 + 99) and with water. The palladium compound was precipitated a second time from a volume of 350 ml and collected in porcelain filtering crucibles. It was thoroughly washed with hot water, dried at 110 C and weighed. The weights of the dried precipitates were 0.1080 g and 0.1051 g, respectively. The calculated quantities of palladium present, using the theoretical factor 0.3167, were 0.0342 g and 0.0333 g.

The filtrates from the second precipitation of the palladium were carefully examined for iridium, by heating them until vapors of sulphuric acid were evolved and adding nitric acid. No iridium was detected in them nor did any rhodium appear to be present, since the solutions remained colorless.

X. SEPARATION OF RHODIUM FROM IRIDIUM

The two metals of the platinum group which remain after the isolation of osmium, of ruthenium, of platinum, and of palladium are rhodium and iridium. These two metals can be separated from each other and determined by the procedure which is described in detail in a previous paper.[27]

Briefly, the method of separation consists in making two precipitations of the rhodium with titanous chloride from a hot solution of the metal sulphates in diluted sulphuric acid (5 + 95). The iridium is recovered from the resulting filtrates, after the removal of titanium with cupferron, by hydrolytic precipitation and determined as metal. The rhodium is recovered by precipitation with hydrogen sulphide, in a solution of the metal sulphate which has been boiled with hydrochloric acid, and is determined as metal.

The determination of rhodium and of iridium can be greatly simplified and the cupferron precipitations avoided if the solution can be divided conveniently into aliquot parts. Since the hydrated dioxides of rhodium and iridium are quantitatively precipitated under the same conditions, the two can be precipitated together and finally recovered as a metallic mixture. In addition, rhodium must be determined separately in a different portion of the solution.

In a forthcoming paper the various procedures of separation and determination which have been developed in this laboratory will be combined into a general scheme of analysis for the platinum group as a whole.

The writer wishes to express his appreciation to Edward Wichers for many helpful suggestions.

WASHINGTON, *December 14, 1933.*

[27] See footnote 9, p. 293.